Episodic Toxicity in the San Francisco Bay System

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Introduction

The Regional Monitoring Program for Trace Substances in the San Francisco Estuary (RMP) has been assessing aquatic toxicity of ambient waters two to three times annually since 1993. The results of the first three years of this monitoring revealed that there was no widespread ambient water toxicity of any significance at the time of these samplings. In winter 1996, RMP sampling coincided for the first time with storm water inflows to the estuary, and significant toxicity to mysid shrimp was detected in water samples from Grizzly Bay, the Sacramento River, and the San Joaquin River (Figure 1). The results of these samples suggested that episodic pulses of contaminants, such as those previously found to be associated with storm water runoff, might be the major cause(s) of any toxicity occurring in the estuary. Sensitive life-stages of numerous resident organisms are present in this portion of the estuary during winter and spring. It is therefore possible that episodic pollution events with important ecological consequences are occurring on time scales that the RMP would not systematically detect. Temporal correlations between ambient water toxicity and the presence of sensitive bay organisms would indicate species at risk, and could serve to focus the development of Best Management Practices to reduce the intensity and duration of toxic episodes or eliminate them altogether. To characterize the extent of the episodic toxicity problem, the RMP initiated a pilot study in late 1996 with the following goals:

- to determine if short-term episodes of significant toxicity are occurring in the estuary,
- to characterize the temporal and spatial distribution of toxic events is, and
- to estimate the duration of toxic episodes.

Study Design and Methods

This pilot study was designed so each year's results can be used to guide the next phase. Initially, the study design contained four sampling stations–two in the northern estuary and two in the extreme South Bay. The 1996—97 stations were Mallard Slough (at Chipps Island) and Napa River (at Mare Island Strait) in the northern estuary, and at Guadalupe Slough and Alviso Slough in the South Bay. The rationale for this sampling approach was two-fold:

- sampling in the northern estuary would complement the Central Valley Regional Board studies, which revealed significant storm water toxicity in the Sacramento River and San Joaquin River watersheds, and the study by Kuivila and Foe (1995), when significant pulses of pesticides associated with storms were entering the northern bay system; and
- sampling in the South Bay would extend 'into the bay' the monitoring coverage of significant toxicity in storm water runoff from local urbanized watersheds (Alameda County Clean Water Program, 1995).

After the results from the first year had been evaluated, the pilot study was expanded to allow for increased sampling frequency at Mallard Slough; beginning in November 1997, samples were taken twice a week and tested for toxicity with the hope of capturing most, if not all, toxic runoff events from the Sacramento River and San Joaquin River watersheds. To complement the South Bay urban watershed monitoring, an additional station for monitoring of storm water runoff into the bay was established at Pacheco Slough, the terminus of the Walnut Creek watershed. The Napa River and Alviso Slough stations were dropped in favor of more frequent sampling at the remaining stations.

Event-directed observations of aquatic toxicity were made using the sensitive crustacean species *Mysidopsis bahia*, following EPA test method 1007. In addition, selected water samples were also analyzed for the organophosphate pesticides diazinon and chlorpyrifos using enzyme-linked immunosorbent assays (ELISAs); these two pesticides have been identified as key causative agents of toxicity in previous studies (e.g., Kuivila and Foe 1995).

DWR is providing access to their sampling station at Mallard Slough on the south side of Chipps Island. This is an ideal location for sampling, as it represents the mixture of upstream waters (from the Sacramento and San Joaquin watersheds) that flow into the northern estuary, and is near the toxicity-testing laboratory in Martinez. Water is pumped directly into sampling containers using the pumping equipment at the site. During winter 1996—97, USGS was also collecting water samples from the Mallard Slough station as part of an investigation of pesticide transport into the northern bay system. As USGS water samples were being analyzed for contaminants, collecting concurrent samples for toxicity testing was an extraordinary opportunity to begin identifying possible causes of any toxicity that we might observe.

In the South Bay, the goal was to sample storm water runoff that had begun to mix with estuarine water (as evidenced by elevated salinity) in Guadalupe Slough and Alviso Slough (Guadalupe River). Decisions on when to sample were made using on-line access to real-time precipitation and runoff data (by the Santa Clara Valley Water District). Sampling in the South Bay was initially accomplished using a 12-foot inflatable vessel that was launched in Guadalupe Slough, and was timed to coincide with high tide when possible in order to facilitate boat access.

Results for 1996—97 Sampling Year

The rainfall pattern in 1996—97 was quite unusual and this influenced the progress of the project. The results of the toxicity tests are summarized Table 1.

Eight water samples were collected concurrently with USGS sampling at the Mallard Island station in December and January. Unfortunately, the first significant rainstorms that winter were severe enough to cause major flooding on the Sacramento and San Joaquin rivers. The scale of this flooding disrupted the usual dormant spray application of pesticides, and as a result, USGS's Suspended Sediment-Pesticide investigation was put on hold after sampling in early January. No toxicity was observed in the baseline water samples which had been collected to that point.

We conserved our testing resources during the winter to sample spring storms, as there is additional pesticide use in the watersheds in late winter and early spring, and previous work had suggested that runoff from spring storms might introduce episodic toxicity into the watersheds. Unfortunately, there were no large spring storms after the early January flooding, with no opportunity to collect samples between January 12 and March 17. The storms sampled in March, April, May, and June were quite small, and did not generate large volumes of runoff. None of these samples were toxic.

In the extreme South Bay, toxicity was observed during three storms, apparently associated with chlorpyrifos concentrations in the range of 70 ng/L or greater (Table 2); chemical analyses of these waters indicated that metals were below toxic concentrations. Additional ELISA samples taken in conjunction with the toxicity tests indicated that pesticide concentrations varied on a very small spatial scale. It appears likely that the toxicity samples, although timed to coincide with episodes of runoff, probably did not coincide with "peak" pesticide concentrations. Characterizing the spatial and temporal extent of such toxicity as it enters the bay thus became a focus of further investigation in 1998.

Results for 1997—98 Sampling Year

While not as extreme as the 96—97 winter flood, the El Niño rainfall this past winter again resulted in a disruption of the normal dormant spray application of pesticides, as well as the normal pattern of intermittent dry periods with periodic rainstorms (it was all pretty much one extended wet spell!).

Mallard Slough. Figure 1 shows the frequency and duration of significant ambient water toxicity observed at Mallard Slough through March 1998. As can be seen, significant occurrences of toxicity to mysids were ob-

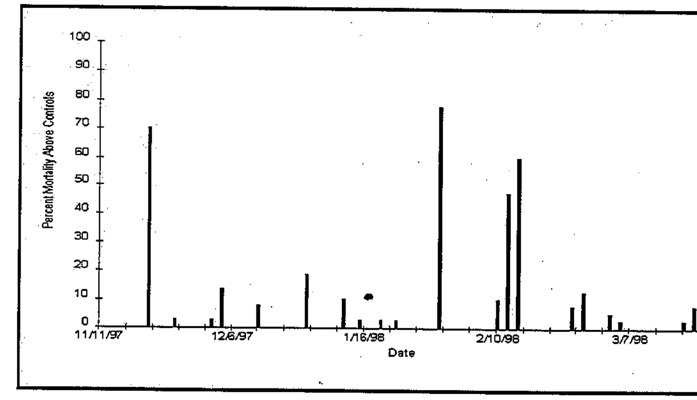

Figure 1. Toxicity at Mallard Island, November 1997 through March 1998

Table 1. Summary of RMP Episodic Toxcity Testing Pilot Project, 1996-1997

	Napa River	Guadalupe Sl/R	Mallard I (USGS*)	Mallard I. (Runoff)
# of Tests	2	16	8	4
# Toxic	0	3	0	0

[a] Sampling was conducted in conjunction with the USGS Honker Bay Project.
[b] Sampling was conducted independently, in response to rainstorm events.

served in November and again in January, indicating that some pulses of toxicity are flowing from the western end of the delta and into the northern estuary, although the duration of the toxicity was very short. A more significant pulse of toxicity was observed in February, in which the toxicity appeared to be present in the bay for at least three days, and possibly for as long as six days.

Interestingly, the mysid toxicity in November and January was in ambient water in which diazinon and chlorpyrifos were both below the method detection limits (~50 ng/L), indicating that the observed toxicity was due to other contaminants. In the case of the extended toxicity observed in February, the water samples collected on February 14, 17, and 19 all had measured diazinon and chlorpyrifos concentrations below the detection limits. However, the water samples collected February 6, 10, and 12 (immediately prior to the toxic water samples) exhibited progressively increasing diazinon concentrations (from 55 ng/l on the February 5 to 116 ng/L on the February 12) indicating that a pulse of diazinon contamination passed through the system immediately prior to the toxic samples. This in turn suggests that a runoff-related pulse of contaminants, some of which reached northern estuary immediately following the diazinon peak, was in fact responsible for the extended toxicity that was observed.

Pacheco Slough. Two of the eight water samples collected at Pacheco Slough were toxic to the mysids, both of which had organophosphate pesticide levels either below the detection limits (in the case of chlorpyrifos) or below the concentration reported to be toxic to *Mysidopsis bahia* (in the case of diazinon). The first toxic sample occurred in early December. The second sample occurred in January at approximately the same time as toxicity was being observed just upstream at Mallard Slough, suggesting that the observed toxicity may have been due to the same contaminants responsible for the upstream toxicity. Our sampling at Pacheco Slough has admittedly been 'hit or miss' with respect to catching contaminant pulses associated with the storm water runoff (the hydrology at this site has yet to be characterized, especially with respect to movement and timing of storm water runoff). Nevertheless, every sample that we have collected from this site has had measurable levels of diazinon, suggesting the presence of a long-term source (e.g., sediments) within the watershed.

South Bay (Guadalupe Slough). Unlike the previous year in which elevated concentrations of chlorpyrifos in storm water runoff were associated with occurrences of toxicity to mysids, there has been no measurable chlorpyrifos or toxicity in any of the Guadalupe Slough water samples collected this winter.

Table 2. Summary of South Bay RMP Episodic Toxicity Pilot Study Testing Results (1996-97)

Site	Sample Collection Date	% Mysid Survival		ELISA Analyses	
		Control	Site Water	Diazinon (ng/L)	Chlorpyrifos (ng/L)
Guadalupe Slough (2 ppt salinity)	10—29—96	97.5	0*	392	145
Guadalupe Slough(4 ppt salinity)	10—29—96	97.5	92.5	b.d.	b.d.
Guadalupe Slough	11—17—96	100	90	n.m.	n.m.
Guadalupe River	11—17—96	100	97.5	n.m.	n.m.
Guadalupe Slough	12—10—96	100	95	176	b.d.
Guadalupe River	12—10—96	100	95	515	67
Guadalupe Slough	1—2—97	100	95	b.d.	b.d.
Guadalupe River	1—2—97	100	95	b.d.	b.d.
Guadalupe Slough	3—17—97	97.5	95	b.d.	b.d.
Alviso Slough	3—17—97	97.5	90	b.d.	b.d.
Guadalupe Slough	4—19—97	95	0*	b.d.	78
Guadalupe River	4—19—97	95	82.5	b.d.	67
Guadalupe Slough	5—23—97	97.5	47.5*	b.d.	70
Guadalupe Rive	5—23—97	97.5	82.5	b.d.	63
Guadalupe Slough	6—4—97	95	100	54	*
Guadalupe River	6—4—97	95	100	74	*

n.m. not measured.
b.d. below detection limits.
* inconsistent results for chlorpyrifos analyses.

Future Plans

The wet seasons of 1996—97 and 1997—98 were both anomalous. In 1998, application of pre-emergent pesticides was disrupted due to an extremely wet February. In addition, the high water flows most likely diluted any pesticide runoff from the agricultural areas of the Central Valley, so that fewer toxic events were observed than during a wet season with low or normal runoff. This is supported by observation of fewer instances of ambient water toxicity upstream as well (Val Connor, personal communication). Therefore, it is probably prudent to maintain the existing sampling scheme in 1998—99.

Given that the RMP baseline toxicity testing has detected ambient water toxicity in summer months as well, it may be desirable to extend such monitoring and toxicity testing throughout the year. Funding to extend the current monitoring for the remaining six months of the year was requested in the 1997 round of CALFED funding, but was turned down. A renewed request for the necessary funding will be resubmitted in any future CALFED funding cycles.

Furthermore, the observation of ambient water toxicity in summer and in winter samples without measurable levels of diazinon or chlorpyrifos is not explained by our current working hypothesis of ambient water toxicity due to seasonal runoff of pesticides. As a result, it would also be desirable to investigate and determine the causes of such toxicity through the application of toxicity identification and evaluation (TIE) methods.

In the South Bay, the focus will continue to be on toxicity due to urban storm water runoff. ELISA analysis of runoff waters collected last season clearly demonstrated that the practice of "grab" samples is 'hit or miss' with respect to catching the peak pesticide concentrations. Therefore, we are proposing to collect composite samples using an autosampler. The on-line access to the runoff monitoring system of the Santa Clara Valley Water District to determine when significant runoff occurs, will enable remote activation of the autosampler to collect composite samples over a 24-hour period. These water samples will be transported to the testing laboratory in Martinez, where diazinon and chlorpyrifos levels will be determined using ELISA, and toxicity evaluated as before.

References

Alameda County Clean Water Program. 1995. Identification and Control of Toxicity in Storm Water Discharges to Urban Creeks: Final Report 1995 for ACURCWP. Alameda County Clean Water Program, Hayward, CA.

Kuivila, K.M. and C.G. Foe. 1995. Concentrations, transport, and biological effects of dormant spray pesticides in the San Francisco Estuary, California. Environ. Toxicol. Chem. 14(7):1141—1150.

X2 Workshop Summary

Wim Kimmerer, SFSU

On March 11, the IEP and the Bay/Delta Modeling Forum sponsored a workshop at Contra Costa Water District in Concord to discuss issues related to the X2 standards and the relationships between X2 and various measures of abundance and survival of fish and invertebrates. X2 is the distance up the axis of the estuary to where tidally-averaged near-bottom salinity is 2 psu. It is considered a measure of physical response of the estuary to changes in freshwater flow, and is being used as a standard for managing the estuary.

A full report about the workshop will be in a future issue of the *Newsletter*. This summary is intended merely as a brief overview of the workshop and the general content of the discussion.

The one-day workshop consisted of presentations by speakers and a panel discussion. Speaker presentations were held in the morning. The following is a list of the presentations and the speakers.

- Introduction—Randy Brown
- Brief History of the Schubel Workshops—Wim Kimmerer
- History of Development of the X2 Standard—Bruce Herbold
- Physics of the Low-Salinity Zone of the Estuary—Jon Burau
- Current Status of the "Fish-X2" Relationships—Wim Kimmerer
- Possible Mechanisms Underlying the Fish-X2 Relationships and Policy Considerations—BJ Miller

The afternoon panel discussion was wide-ranging, and included such topics as future research needs and possible alternatives to X2 as a standard.